

Molecular Modeling of Silicon-Based Anode Material for High-Performance Lithium-Ion Batteries

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ABSTRACT

Silicon(Si)-based anode materials for lithium-ion batteries (LIB) have been attracting much attention due the high theoretical capacity of Si. There exist, however, some limitations preventing a wide usage and application of Si-electrodes. Material pulverization, morphology and volume changes and a reduced solid-electrolyte interphase stability are critical challenges that need to be addressed for improving the performance of Si-based electrodes. Nanostructured Si materials have been developed to overcome these issues.

Here, we address mechanical properties of porous carbon-coated Si which are important for the stability and durability of the Si anode material. Molecular dynamics (MD) simulations have been performed to model regular micro- and mesoporous Si as well as amorphous porous Si. Carbon has been inserted into the porous Si structures and we have systematically analyzed how pore size, carbon coating, and defects in the coating affect the elasticity of the material by calculating Young's modulus. Our results show that the mechanical properties are influenced by the carbon coating and suggest that it can be used to tune the stability of this important class of electrode material.

Keywords: nanostructured anode material, porous Si, carbon coating, mechanical properties, molecular modeling

1 INTRODUCTION

Industrial needs and consumer demands require powerful energy storage systems. among which batteries play a central role. Lithium(Li)-ion batteries are widely used in portable electronic devices. Their use as energy storage system in other important industrial fields - such as electric vehicles, wind turbines, or photo voltaic plants - is limited by their storage capacity. The latter is governed by the electrode material [1]. To satisfy the increasing requirements of industry and consumers, new kinds of powerful anode materials need to be developed.

Silicon (Si) is regarded as next-generation anode material for several reasons: It's theoretical capacity is more than ten times higher compared to graphite which is used for state-of-the art battery anodes. Moreover, Si combines low cost and low toxicity with a high abundance [2]. Despite many beneficial key characteristics, pure Si-based

electrodes have, however, one major drawback: They experience large volume changes during charging and discharging which induces pulverization of the electrode and fast fading of the capacity [3]. The large volume changes also affect the formation of a passivating solid-electrolyte interface which reduces the Coulombic efficiency [4,5]. In order to overcome these problems, different kinds of nanostructured Si materials have been designed. Promising approaches range from porous over composite to core-shell structures and it has been shown that these materials improve the performance significantly [see e.g. 1-7 and references therein]. It could be shown experimentally that carbon-coated porous Si shows an enhanced specific capacity and improved cycling performance [4].

Pulverization and morphology or volume changes of plain Si electrodes lead not only to performance losses, but also to mechanical instability. Since porous Si and also carbon-coated porous Si is regarded as promising material for anodes in LIBs, it is important to investigate the mechanical properties of these material classes.

In the following, we will show that molecular modeling is ideally suited to systematically study mechanical properties of nanostructured Si-based anode materials. We have performed molecular dynamics simulations for modeling regular micro- and mesoporous Si. In addition, amorphous porous Si has been modeled. Based on these porous Si structures, we have systematically studied how pore size, carbon coating and defects in the coating influence the mechanical properties by calculating Young's modulus. Our results show that carbon coating can enhance the mechanical stability of this material class which can be exploited to tune the properties of this promising next-generation anode material.

2 RESULTS AND DISCUSSION

To study the mechanical properties of nanostructured Si materials, structures of porous Si with regular pores were modeled for different pore radii ranging from 7 up to 50 Å (denoted as structure set (A)). Details on how the initial structures were built and the simulation set-up can be found in the Computational Details section. In addition, an amorphous porous Si structure was modeled (denoted as structure set (B)). In the equilibrated structures, carbon was inserted as carbon nanotubes (CNTs) and atom-wise in

structure set (A) and (B), respectively. In Figure 1, a representative example of a CNT-coated Si pore is shown.

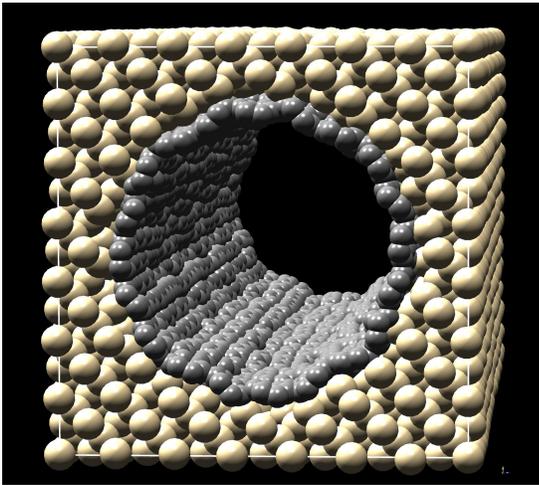


Figure 1: Model structure of CNT-coated Si pore.

Defect structures of the CNT-coated models were created by randomly removing up to 25 % of carbon atoms.

2.1 Structural Properties

First, the structural properties of structure set (A) will be discussed. The density profiles of the carbon coating perpendicular to the pores have been analyzed for the intact structures and structures from which 10 % carbon atoms have been removed. The maximum density at the C-Si interface is reduced and the maximum peaks move closer together indicating that the defects cause a shrinking of the pore. The density profiles of double-coated pores (i. e. in which two CNTs have been inserted) from which up to 25 % of carbon atoms have been removed are shown in Figure 2.

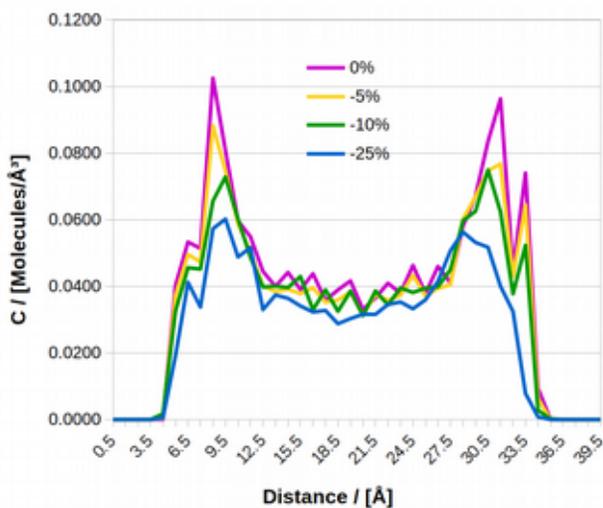


Figure 2: Density profile of carbon in double CNT-coated pores from which up to 25 % carbon atoms have been removed.

These findings are in line with the pore size analysis which provides the diameter of the largest probe sphere that can be placed in the pore. This diameter reduces when defects are introduced. In case of the double coated pore, it reduces from 18.7 to 14.2 Å when going from the intact structure to the structure in which 25 % carbon have been removed. In the amorphous structures, the largest included sphere becomes slightly larger when carbon is introduced. The diameter of the largest included sphere increases from 16.1 to 21.2 Å. The increase in the diameter of the largest included sphere is not a function of the number of inserted carbon atoms, since the largest cavity was found in a structure with a medium number of added carbon atoms. Since however larger pores are consistently found in carbon-coated structures, the pore analysis indicates, however, a stabilizing influence of carbon on the porous structure.

The results of the ring size analysis are summarized in Table 1.

	Loops of size			
	4	5	6	7
Si-r7-cnt8	0	0	728	0
Si-r10-cnt14	0	0	1276	0
Si-r10-cnt14-10	0	9	690	3
Si-r14-cnt20	0	0	1756	0
Si-r14-cnt20-10	0	5	937	1
Si-r14-cnt20-cnt17	24	1	3393	9
Si-r14-cnt20-cnt17-5	13	4	2461	10
Si-r14-cnt20-cnt17-10	3	14	1846	29
Si-r14-cnt20-cnt17-25	1	20	732	69
Si-r25-cnt34	0	0	5972	0
Si-r50-cnt71	0	0	12496	0
Si-r50-cnt71-10	0	20	6633	14
a-Si-C19500	0	9	113	36
a-Si-C13000	0	4	27	5
a-Si-C6500	0	0	0	0

Table 1: Ring size analysis of carbon structures in regular and amorphous porous Si models. The nomenclature is described in the Computational Details section.

The vast majority of rings consists of 6-membered rings as could be expected. Defects consequently decrease the number of 6-membered rings in favor for 4-, 5-, and 7-membered rings. Amorphous structures are intrinsically less regular compared to the models of set (A). In addition, the C:Si ratio is rather small. For these reasons, the number of ring structures is significantly reduced compared to the regular structures. The ring size analysis shows that 6-membered rings are preferred while the absolute number of ring structures is small and most carbon atoms are not part of ring structures in these models.

2.2 Mechanical Properties

For investigating how the mechanical properties depend on the pore size and composition, tensile stress was applied

along the pore and the elastic moduli were obtained from the corresponding stress-strain curves. For comparison, Young's modulus was also determined perpendicular to the pore. The results for the regular pores are summarized in Figure 3.

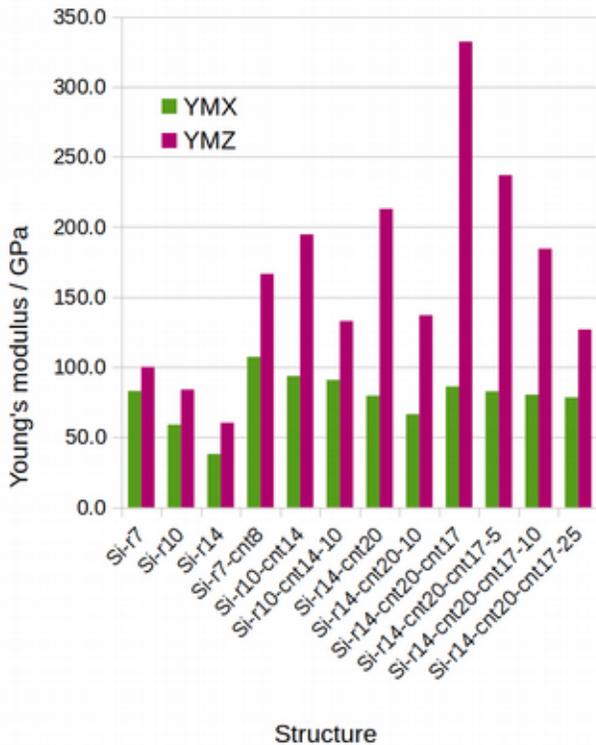


Figure 3: Young's modulus in GPa for various regular pure and carbon-coated Si pores.

For pure Si pores, the elastic modulus decreases along x and z direction with increasing pore size. Carbon-coating increases the elastic modulus compared to the pure pores. Along x direction, Young's modulus becomes smaller with increasing pore size as observed for the uncoated pores. Along z direction, Young's modulus the behavior is different and it increases with increasing pore size. Increasing the tensile stress up to 20 % indicates plastic deformation or even rupture was observed except for Si-r14-cnt20. After repeating the simulation five times, rupture was observed in three out of five runs.

For pores with a radius of 25 and 50 Å similar trends are observed. For Si-r25, an elastic modulus of 99.7 GPa was obtained, which is reduced to 58.1 GPa in Si-r50. Carbon-coating increases Young's modulus to 121.5 and 110.7 GPa for Si-r25-cnt34 and Si-r50-cnt71, respectively. Introducing defects reduces the elastic modulus again and for Si-r50-cnt71-10 a modulus of 81.6 GPa was obtained.

The amorphous systems show a significantly reduced stiffness compared to the regular pores which can be attributed to the less ordered structure. The elastic moduli along x and z direction for amorphous models are illustrated in Figure 4.

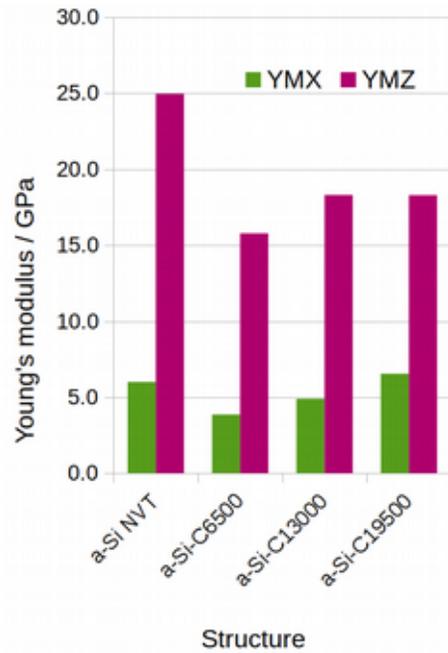


Figure 4: Young's modulus in GPa for different amorphous porous Si models.

The largest value is obtained for the amorphous system without any carbon along z direction. In contrast to the regular structures, the stiffness is not increased by carbon coating, but with increasing carbon content Young's modulus increases. This has been found for both directions x and z.

3 COMPUTATIONAL DETAILS

All model structures have been build using Scientomics MAPS software platform [8] which was also used for setting up and analyzing simulations. Molecular Dynamics simulations were performed using LAMMPS [9]. The script polypy [10] was used for additional ring size analysis.

Two types of porous silicon (Si) models were created: (A) regular Si pores and (B) amorphous porous Si. For building structures of type (A), a Si supercell was built along cell parameters a and b of crystalline Si and all atoms within a certain radius from the the central atoms were removed. Then a supercell along cell parameter c was built. Models of different pore size and cell lengths have been created to study regular pores: (i) Simulation cells with pore radii of 7, 10 and 14 Å and cell dimensions of 38x38x114 Å and (ii) simulation cells of with pore radii of 14, 25 and 50 Å and cell dimensions of 38x38x114 Å have been created. The structures are labeled as Si-r7, Si-r10, Si-r14, etc. In these structures, carbon-nanotubes (CNTs) were inserted. Chiral vectors of (n,m) = (8,8), (14,14), (20,20) were used to build CNTs for Si-r7, Si-r10, and Si-r14, respectively. CNT-containing Si structures are labeled as Si-r7-cnt8, etc. In addition, one model based on Si-r14 containing two CNTs with (n,m) = (20,20) and (17,17) was

created. For simulation cells of series (ii), CNTs with $(n,m) = (34,34)$ and $(71,71)$ have been inserted into Si-r25 and Si-r50, respectively. In addition to pristine structures, defect structures were created for Si-r10, Si-r10, Si-r14, and Si-r50 by randomly removing 10 % carbon atoms. For the model system containing two CNTs, 5, 10, and 25 % of carbon atoms were randomly removed to introduce defects. Corresponding structures are labeled as Si-r10-cnt14-10, etc.

Molecular dynamics simulations have been performed using LAMMPS and a Si-C Tersoff potential parametrized by Erhart and Albe [11]. First, an equilibration at 298 K and 1 atm over one 1 ns using NPT conditions was performed. The final structures served as models for studying elastic deformation using non-equilibrium dynamics. For these type of simulations, the cell in z direction was continuously increased up to 5% of the original size over 1 ns. The elastic modulus was obtained from the slope of the stress-strain curve. Additional tensile stress simulations in which the cell was stretched along x direction was performed for a subset (Si-r7, Si-r10, and Si-r14). For this subset, simulations increasing the cell length in z direction up to 20 % were carried out to study the elastic limit.

Amorphous porous silicon models were created building a supercell along cell parameters a and b of crystalline Si and randomly removing 2113 atoms. The number of atoms was chosen to roughly introduce the same void volume as in Si-r50. After removing Si atoms, a supercell along z was built so. The final cell with dimensions of $23 \times 23 \times 40$ Å contained 84760 atoms. The structure was first equilibrated over 1 ns at 298 K and 1 atm using NVT conditions. Subsequently, a NPT equilibration over 2 ns was performed. Elastic deformation was studied by increasing the cell size up to 5 % of the initial size during a 1 ns non-equilibrium MD simulation. For creating carbon-coated systems, the final conformation after 1 ns of the NPT equilibration was used from which all non-bonded Si atoms have been removed. Three models with different amounts of carbon were created by inserting (i) 6500, (ii) 13000, and (iii) 19500 carbon atoms MAPS Amorphous builder. The structures have been equilibrated over 1 ns at 298 K and 1 atm using NVT conditions, before performing non-equilibrium MD simulations as described above and applying 5 % tensile stress to study mechanical properties of the amorphous system.

4 CONCLUSION

Porous Si belongs to a class of highly promising next-generation anode materials for LIBs. We have systematically analyzed how the structural and mechanical properties are affected by pore size and composition. For regular micro- and mesoporous systems, similar trends have been observed and our results show that carbon-coating can be used to tune the elastic properties. Less pronounced effects have been found for amorphous systems, for which

however also a clear influence of introduced carbon on the mechanical properties could be shown.

Overall our results, help get a better understanding of the material properties and how they can be tuned in the desired direction.

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